

PATENT COOPERATION TREATY

PCT

NOTIFICATION OF ELECTION

(PCT Rule 61.2)

From the INTERNATIONAL BUREAU

To:

Commissioner
 US Department of Commerce
 United States Patent and Trademark
 Office, PCT
 2011 South Clark Place Room
 CP2/5C24
 Arlington, VA 22202
 ETATS-UNIS D'AMERIQUE
 in its capacity as elected Office

Date of mailing (day/month/year) 02 May 2001 (02.05.01)	
International application No. PCT/GB00/03211	Applicant's or agent's file reference 15431 MdCm
International filing date (day/month/year) 18 August 2000 (18.08.00)	Priority date (day/month/year) 21 August 1999 (21.08.99)
Applicant MACKLIN, William, James et al	

1. The designated Office is hereby notified of its election made:

☒ in the demand filed with the International Preliminary Examining Authority on:
 17 February 2001 (17.02.01)

☐ in a notice effecting later election filed with the International Bureau on:

2. The election ☒ was

☐ was not

made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland Facsimile No.: (41-22) 740.14.35	Authorized officer Olivia TEFY Telephone No.: (41-22) 338.83.38
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PATENT COOPERATION TREATY

PCT

NOTIFICATION OF THE RECORDING
OF A CHANGE(PCT Rule 92bis.1 and
Administrative Instructions, Section 422)

From the INTERNATIONAL BUREAU

To:

MANSFIELD, Peter, Turquand
Patents Department
Accentus plc
329 Harwell
Didcot
Oxfordshire OX11 0QJ
ROYAUME-UNI

Date of mailing (day/month/year) 21 August 2001 (21.08.01)	IMPORTANT NOTIFICATION International filing date (day/month/year) 18 August 2000 (18.08.00)
Applicant's or agent's file reference 15431 MdCm	
International application No. PCT/GB00/03211	

1. The following indications appeared on record concerning:

☐ the applicant ☐ the inventor ☒ the agent ☐ the common representative

Name and Address MANSFIELD, Peter, Turquand AEA Technology plc Patents Dept. 329 Harwell Didcot Oxfordshire OX11 0QJ United Kingdom	State of Nationality	State of Residence
	Telephone No. 01235 43 2037	
	Facsimile No. 01235 43 6658	
	Teleprinter No.	

2. The International Bureau hereby notifies the applicant that the following change has been recorded concerning:

☐ the person ☐ the name ☒ the address ☐ the nationality ☐ the residence

Name and Address MANSFIELD, Peter, Turquand Patents Department Accentus plc 329 Harwell Didcot Oxfordshire OX11 0QJ United Kingdom	State of Nationality	State of Residence
	Telephone No. 01235 43 2037	
	Facsimile No. 01235 43 6658	
	Teleprinter No.	

3. Further observations, if necessary:

4. A copy of this notification has been sent to:

<input checked="" type="checkbox"/> the receiving Office	<input type="checkbox"/> the designated Offices concerned
<input type="checkbox"/> the International Searching Authority	<input checked="" type="checkbox"/> the elected Offices concerned
<input checked="" type="checkbox"/> the International Preliminary Examining Authority	<input type="checkbox"/> other:

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland Facsimile No.: (41-22) 740.14.35	Authorized officer R. Raissi Telephone No.: (41-22) 338.83.38
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repeated insertion and removal of lithium into bulk tin metal tends to show poor reversibility due to large volumetric changes, improved stability of tin oxide anodes is observed due to the presence of an oxide framework surrounding the metallic tin particles.

According to the present invention an anode for a rechargeable lithium cell comprises carbon nanotubes that contain within them a metal or a metalloid that can form alloys reversibly with lithium over a range of compositions.

Preferably the metal or metalloid within the nanotubes is a metallic element such as aluminium or tin, or a metallic alloy such as antimony/tin, but it may also be possible for it to be a metalloid such as silicon. The term alloy should be understood as encompassing both conventional alloys and lithium/elemental compounds of the general formula MLi_x , where M represents the other element (metal or metalloid) and x may have a range of different values.

Preferably the carbon nanotubes are bound together by a polymeric binder, which may for example be polyvinylidene fluoride.

The present invention also provides a rechargeable lithium cell incorporating an anode as specified above, a reversible cathode, and an electrolyte. The electrolyte may be either a solid polymeric electrolyte, or a liquid electrolyte. Where the electrolyte is a liquid, an inert, liquid-permeable separator is usually provided to

separate the anode from the cathode. A variety of different intercalation materials may be used in such a cathode.

5 Such a cell can be expected to have improved capacity and improved reversibility, because the nanotubes will provide a stabilising framework for the alloy. The carbon nanotubes may also provide additional lithium intercalation capacity.

10

Carbon nanotubes are tube-like structures of diameter no more than a few nanometres, but which may be several microns in length. They can be considered as a sheet or hexagonal lattice of carbon atoms (as in a layer
15 of graphite) which has been rolled up to make a cylinder, with a hemispherical cap like half a fullerene molecule at each end. The nanotubes can be characterized by their diameter, and their helicity, which is determined by the axis about which the sheet is rolled. They have been made
20 by laser vaporisation of a carbon target in a furnace, in the presence of a cobalt/nickel catalyst; they have also been made using a carbon arc.

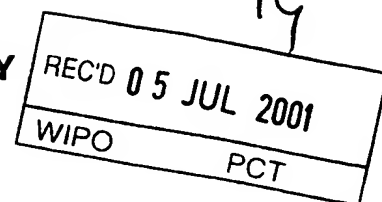
The invention will now be further and more
25 particularly described, by way of example only. Carbon nanotubes are prepared electrolytically, by using a carbon electrode as cathode in a bath of molten salt, such as sodium chloride. It is believed that, on the application of current, sodium is forced into the
30 graphite structure and this induces the extrusion of the nanotubes. A less stable salt, such as tin chloride, is also introduced into the molten salt bath. This decomposes first, and the resulting metal (tin) is

Claims

1. An anode for a rechargeable lithium cell, the anode comprising carbon nanotubes, characterized in that the
5 nanotubes contain within them a metal or a metalloid that can form alloys reversibly with lithium over a range of compositions.
2. An anode as claimed in claim 1 wherein the metal or
10 metalloid is selected from: aluminium, tin, metallic alloys containing aluminium or tin, or silicon.
3. An anode as claimed in claim 1 or claim 2 wherein
15 the carbon nanotubes are bound together by a polymeric binder.
4. An anode as claimed in claim 3 comprising both a polymeric binder and a plasticising solvent.
- 20 5. A rechargeable lithium cell incorporating an anode as claimed in any one of the preceding claims, a reversible cathode, and an electrolyte.

PATENT COOPERATION TREATY

PCT



INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference 15431 MdCm	FOR FURTHER ACTION See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. PCT/GB00/03211	International filing date (day/month/year) 18/08/2000	Priority date (day/month/year) 21/08/1999
International Patent Classification (IPC) or national classification and IPC H01M4/58		
Applicant AEA TECHNOLOGY PLC		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.



2. This REPORT consists of a total of 5 sheets, including this cover sheet.

- ☒ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consist of a total of 4 sheets.

3. This report contains indications relating to the following items:

- I ☒ Basis of the report
- II ☐ Priority
- III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- IV ☐ Lack of unity of invention
- V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI ☐ Certain documents cited
- VII ☐ Certain defects in the international application
- VIII ☐ Certain observations on the international application

Date of submission of the demand 17/02/2001	Date of completion of this report 03.07.2001
Name and mailing address of the international preliminary examining authority:  European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized officer Haering, C Telephone No. +49 89 2399 8010 

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/GB00/03211

I. Basis of the report

1. With regard to the **elements** of the international application (*Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17)*):

Description, pages:

1,4-6	as originally filed		
2,2a,3	as received on	18/06/2001	with letter of 13/06/2001

Claims, No.:

1-4	as received on	18/06/2001	with letter of 13/06/2001
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2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
- ☐ the language of publication of the international application (under Rule 48.3(b)).
- ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.
- ☐ filed together with the international application in computer readable form.
- ☐ furnished subsequently to this Authority in written form.
- ☐ furnished subsequently to this Authority in computer readable form.
- ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
- ☐ the claims, Nos.:
- ☐ the drawings, sheets:

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. **PCT/GB00/03211**

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

6. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	1-4
	No:	Claims	
Inventive step (IS)	Yes:	Claims	1-4
	No:	Claims	
Industrial applicability (IA)	Yes:	Claims	1-4
	No:	Claims	

- 2. Citations and explanations**
see separate sheet

Re Item V

Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Disclosures:

- D1: CHE G ET AL, NATURE vol. 393, no. 6683, pages 346-349, XP000960755
D2: PATENT ABSTRACTS OF JAPAN JP 09 045312 A
D3: PATENT ABSTRACTS OF JAPAN JP 10 125321 A
D4: CHE G ET AL, LANGMUIR, vol. 15, no. 3, 1999, pages 750-758, XP000964916
D5: FRACKOWIAK E ET AL, CARBON, vol. 37, no. 1, 1999, pages 61-69, XP000964865
D6: LOISEAU A ET AL, CHEMICAL PHYSICS LETTERS, 1996, pages 246-252, XP000972665
D7: GUERRET-PLECOURT C ET AL, NATURE vol. 372, no. 6508, pages 761-764, XP000569346
- 1.1. Document D1 (p.348, the three first paragraphs) and D2 (pages 756, right-hand column to 758, left-hand column) both disclose an anode for a lithium cell, comprising carbon nanotubes, with Fe-catalysed carbon nanotubes contained within (tube-in-tube membrane). Those nanotubes are capable of intercalating Li⁺-ions. High energy density is thus obtained. **Fe** is used as a catalyser for the synthesis of the tube-in-tube nanostructured carbon material, but **is not there to form alloys with th lithium.**
- 1.2. D3 discloses a secondary lithium cell having an anode comprising carbon nanotubes that contain within them at least one kind of elements of Li, Na, K, Mg or Ca. High energy density is thus obtained.
- 1.3. Documents D4 and D5 both disclose an anode for a lithium cell comprising pure carbon nanotubes, i.e. **without metal or metalloid.**
- 1.4. Documents D6 and D7 both disclose the synthesis of carbon nanotubes that contain nanowires of different elements, for example Al (D6, abstract), Si (D6, abstract) or Sn (D6, D7, abstracts). **No us of th synth sised nanotubes is m ntioned.** Thus, those documents are not considered to be relevant.

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/GB00/03211

2. Novelty:

- 2.1. The subject-matter of claim 1 is novel over the known prior art (see 1.1. to 1.4.). The addition of polymeric binder alone (claim 3), or with a plasticising solvent (claim 4) is novel over the prior art too.
- 2.2. A rechargeable lithium cell according to claim 4, incorporating an anode as claimed in any of the preceding claims, is a fortiori novel too.

3. Inventive step:

- 3.1. Documents D1 and D2 are not relevant for the question of inventive step for the subject-matter of claims 1 to 4; indeed, the iron present in the nanotubes, and not Sn, Al, Si, or combination of, permits the synthesis of the tube-in-tube nanostructured carbon material, but is not there to form alloys with the lithium (MLi_x).

- 3.2. Document D3, which is considered to represent the most relevant state of the art, discloses (cf. 1.1.) an anode for a lithium cell from which the subject-matter of claim 2 differs in that the carbon nanotubes contain a metal (or metalloid) selected from Al, Sn or alloys of, or Si.

The problem to be solved by the present invention may be regarded as increasing the capacity and the reversibility of the lithium cell.

The problem is only partially solved by D3, wherein the nanotubes contain some metal(s), like Li, Na, K, Mg or Ca, because:

- the concentration of the metal(s) is very low, i.e. the carbon structure is doped,
- the elements were especially selected for their low ionisation potential [0007].

- 3.3. Thus, it is not obvious for the person skilled to select other metals or metalloid(s) within its carbon nanotubes to further increase the cell's capacity.

As a consequence, the subject-matter of claim 1 is considered to involve an inventive step with respect of the disclosure of the known prior art under Article 33(1) and (3) PCT.

A fortiori, the subject-matters of claims 2 to 4 are also considered to be inventive.

INTERNATIONAL SEARCH REPORT

Inter. Application No

PCT/GB 00/03211

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 H01M4/58 C01B31/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 H01M C01B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, CHEM ABS Data, INSPEC, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CHE G ET AL: "CARBON NANOTUBULE MEMBRANES FOR ELECTROCHEMICAL ENERGY STORAGE AND PRODUCTION" NATURE, MACMILLAN JOURNALS LTD. LONDON, GB, vol. 393, no. 6683, 28 May 1998 (1998-05-28), pages 346-349, XP000960755 ISSN: 0028-0836 the whole document	1, 3-5
X	CHE G ET AL: "METAL-NANOCLUSTER-FILLED CARBON NANOTUBES: CATALYTIC PROPERTIES AND POSSIBLE APPLICATION IN ELECTROCHEMICAL ENERGY STORAGE AND PRODUCTION" LANGMUIR, vol. 15, no. 3, 1999, pages 750-758, XP000964916 the whole document	1, 3-5

☒ Further documents are listed in the continuation of box C.

☐ Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *&* document member of the same patent family

Date of the actual completion of the international search

18 December 2000

Date of mailing of the international search report

28/12/2000

Name and mailing address of the ISA

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Authorized officer

Riba Vilanova, M

INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 00/03211

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PATENT ABSTRACTS OF JAPAN vol. 1997, no. 06, 30 June 1997 (1997-06-30) -& JP 09 045312 A (MATSUSHITA ELECTRIC IND CO LTD), 14 February 1997 (1997-02-14) abstract ---	1,3-5
A	FRACKOWIAK E ET AL: "ELECTROCHEMICAL STORAGE OF LITHIUM MULTIWALLED CARBON NANOTUBES" CARBON, vol. 37, no. 1, 1999, pages 61-69, XP000964865 the whole document ---	1-5
A	PATENT ABSTRACTS OF JAPAN vol. 1998, no. 10, 31 August 1998 (1998-08-31) & JP 10 125321 A (SONY CORP), 15 May 1998 (1998-05-15) abstract ---	1-5
A	LOISEAU A ET AL: "Synthesis of long carbon nanotubes filled with Se, S, Sb and Ge by the arc method" CHEMICAL PHYSICS LETTERS, 1996, pages 246-252, XP000972665 abstract Section "1. Introduction" Section "4. Conclusion" ---	1,2
A	GUERRET-PLECOURT C ET AL: "RELATION BETWEEN METAL ELECTRONIC STRUCTURE AND MORPHOLOGY OF METALCOMPOUNDS INSIDE CARBON NANOTUBES" NATURE,GB,MACMILLAN JOURNALS LTD. LONDON, vol. 372, no. 6508, 22 December 1994 (1994-12-22), pages 761-764, XP000569346 ISSN: 0028-0836 abstract -----	1,2

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 00/03211

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
JP 09045312 A	14-02-1997	NONE	
JP 10125321 A	15-05-1998	NONE	